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<b>13. SUPPLEMENTARY NOTES</b>						
<b>14. ABSTRACT</b> <p>During the current grant period we have made substantial progress. We have been applying ultrafast 2D IR vibrational echo spectroscopy to important problems of molecular dynamics; we have been using a variety of techniques to study room temperature ionic liquids (RTILs); and we have advanced the early stages of investigation of interfacial and surface phenomena using ultrafast IR spectroscopy. We made a major theoretical advance in how to analyze ultrafast 2D IR vibrational echo spectral diffusion data. We further developed and applied 2D IR Vibrational Echo Chemical Exchange Spectroscopy, which we pioneered during the last AFOSR grant period. We have also been studying RTILs using optical heterodyne detected optical Kerr Effect measurements, time resolved fluorescence spectroscopy, and initial experiments directed to using 2D IR vibrational echo spectroscopy. Of particular importance we have realized a main new thrust of the work, that is, we have performed the first investigations of the dynamics of a heterogeneous catalyst using ultrafast infrared vibration echo spectroscopy of a submonolayer of molecules. Ultrafast two-dimensional infrared vibrational echo spectroscopy has proven broadly useful for studying molecular dynamics in solutions. We exte</p>						
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## **A. Ultrafast Infrared and Other Experiments and Theory of Complex Liquids**

### **1. New Theoretical Method for Analysis of 2D IR Vibrational Echo Data<sup>1</sup>**

Ultrafast two-dimensional infrared (2D IR) vibrational echo spectroscopy can probe the fast structural evolution of molecular systems under thermal equilibrium conditions. Structural dynamics are tracked by observing the time evolution of the 2D IR spectrum, which is caused by frequency fluctuations of vibrational mode(s) excited during the experiment. Until recently, it was necessary to calculate the 2D spectrum and then iteratively fit it. We developed a theoretical method for extracting the frequency-frequency correlation function (FFCF) from 2D IR spectra. We have reduced the fitting process from days to minutes. In addition, there are a variety of effects that can produce line shape distortions and prevent the correct determination of the FFCF, which describes the frequency fluctuations and connects the experimental observables to a molecular level depiction of dynamics. The experimental observable is the center line slope (CLS) of the 2D IR spectrum. CLS is immune to line shape distortions caused by destructive interference between bands arising from vibrational echo emission from the 0-1 vibrational transition (positive) and from the 1-2 vibrational transition (negative) in the 2D IR spectrum. Also, line shape distortions caused by solvent background absorption and finite pulse durations do not affect the determination of the FFCF with the CLS method. The CLS method is now being widely used by both experimentalists and theoreticians for 2D IR spectral analysis.

### **2. Ultrafast 2D IR Vibrational Echo Chemical Exchange Spectroscopy<sup>9</sup>**

Under AFOSR sponsorship, the Fayer group pioneered the 2D IR Vibrational Echo Chemical Exchange spectroscopy. This method permits the examination of chemical kinetics between species under thermal equilibrium kinetics. In a Chemical Exchange Spectroscopy experiment, different species produce peaks in the 2D spectrum on the diagonal. Chemical exchange between two or more species manifests itself as the growth of off-diagonal peaks. The time dependence of the growth of the peaks provides a direct measurement of the interconversion between the species without perturbing the thermal equilibrium.

#### **a. Ion-Water Hydrogen Bond Switching<sup>2</sup>**

The exchange of water hydroxyl hydrogen bonds between anions and water oxygens was observed directly with ultrafast 2D IR vibrational echo chemical exchange spectroscopy. The OD hydroxyl stretch of dilute HOD in H<sub>2</sub>O in concentrated (6 M) aqueous solutions of sodium tetrafluoroborate (NaBF<sub>4</sub>) displays a spectrum with a broad water-like band (hydroxyl bound to water oxygen) and a resolved, blue shifted band (hydroxyl bound to BF<sub>4</sub><sup>-</sup>). The growth of the chemical exchange peaks in the 2D IR spectrum yields the time dependence of anion-water hydroxyl hydrogen bond switching under thermal equilibrium conditions as  $\tau = 7 \pm 1$  ps. This is the first direct measurement of hydrogen bond exchange.

### **b. Solute-Solvent Complex Switching Dynamics<sup>3</sup>**

Hydrogen bonds formed between C-H and various hydrogen bond acceptors play important roles in the mechanisms of C-H bond cleavage reactions, and the structures of proteins and organic crystals. Chloroform, a C-H hydrogen bond donor, can form weak hydrogen bonded complexes with acetone and with dimethylsulfoxide (DMSO). When chloroform is dissolved in a mixed solvent consisting of acetone and DMSO, both types of hydrogen bonded complexes exist. The two complexes, chloroform-acetone and chloroform-DMSO, are in equilibrium, and they rapidly interconvert by chloroform exchanging hydrogen bond acceptors. This fast hydrogen bond acceptor substitution reaction was explicated using vibrational echo chemical exchange spectroscopy.

### **c. Hydrogen Bond Migration between Molecular Sites<sup>4</sup>**

Hydrogen bonded complexes between phenol and phenylacetylene were studied using 2D IR chemical exchange spectroscopy. Phenylacetylene has two possible  $\pi$  hydrogen bonding acceptor sites (phenyl or acetylene) that compete for hydrogen bond donors in solution at room temperature. The appearance of off-diagonal peaks between the two vibrational frequencies in the 2D IR spectrum reports on the exchange process between the two competitive hydrogen bonding sites of phenol-phenylacetylene complexes in the neat phenylacetylene solvent. The chemical exchange process occurs in  $\sim 5$  ps, and was assigned to direct hydrogen bond migration along the phenylacetylene molecule. The observation of direct hydrogen bond migration has important implications for macromolecular systems.

### **d. Solute-Solvent Complex Kinetics and Thermodynamics<sup>5</sup>**

The formation and dissociation kinetics of a series of triethylsilanol/solvent weakly hydrogen bonding complexes with enthalpies of formation ranging from  $-1.4$  kcal/mol to  $-3.3$  kcal/mol were measured with chemical exchange spectroscopy in liquid solutions at room temperature. The correlation between the complex enthalpies of formation and dissociation rate constants can be expressed with an equation similar to the Arrhenius equation. It was found that the inverse of the solute-solvent complex dissociation rate is linearly related to  $\exp(-\Delta H_0/RT)$  where  $\Delta H_0$  is the complex enthalpy of formation. It was shown that the triethylsilanol-solvent complexes obey the same relationship with the identical proportionality constant as eight phenol complexes.

### **e. Direct Observation of Fast Protein Conformational Switching<sup>6</sup>**

The methods developed for study of liquids were transferred to an important biological problem. Folded proteins can exist in multiple conformational substates. Each substate reflects a local minimum on the free energy landscape with a distinct structure. Using vibrational echo chemical exchange spectroscopy, conformational switching between two well-defined substates of a myoglobin mutant was observed with a 47 ps time constant. The results demonstrate that interconversion between protein

conformational substates can occur on very fast time scales. The implications for larger structural changes that occur on much longer time scales were discussed.

### **3. Ultrafast Studies of Water Systems**

#### **a. The Effects of Ions, Nanoconfinement, and Interfaces<sup>7,8</sup>**

Hydrogen bond dynamics of water in highly concentrated NaBr salt solutions and reverse micelles were studied using ultrafast 2D IR vibrational echo spectroscopy and polarization selective IR pump-probe experiments performed on the OD hydroxyl stretch of dilute HOD in H<sub>2</sub>O. The vibrational echo experiments measure spectral diffusion and the pump-probe experiments measure orientational relaxation. Both experimental observables are directly related to the structural dynamics of water's hydrogen bond network. The measurements performed on NaBr solutions as a function of concentration show that the hydrogen bond dynamics slow as the NaBr concentration increases. Complete hydrogen bond randomization slows by a factor of ~3 in 6 M NaBr solution compared to bulk water. Hydrogen bond dynamics of water in nanoscopically confined environments were studied by encapsulating water molecules in ionic head group (AOT) and non-ionic head group (Igepal CO 520) reverse micelles. Water dynamics in the nanopools of AOT reverse micelles were studied as a function of size by observing orientational relaxation. Orientational relaxation dynamics deviate significantly from bulk water. To determine if the changes in dynamics from bulk water are caused by the influence of the ionic head groups of AOT or the nanoconfinement, the water dynamics in nanopools in AOT reverse micelles (ionic) and Igepal reverse micelles (non-ionic) were compared. It was found that the water orientational relaxation in the two types of reverse micelles is very similar, which indicates that confinement by an interface is a primary factor governing the dynamics of nanoscopic water rather than the presence of charged groups at the interface.

#### **b. Water Inertial Reorientation: Hydrogen Bond Strength and the Angular Potential<sup>10</sup>**

The short time orientational relaxation of water was studied by ultrafast infrared pump-probe spectroscopy of the hydroxyl stretching mode (OD of dilute HOD in H<sub>2</sub>O). The anisotropy decay displays a sharp drop at very short times caused by inertial orientational motion, followed by a much slower decay that fully randomizes the orientation. Investigation of temperatures from 1 °C to 65 °C showed that the amplitude of the inertial component (extent of inertial angular displacement) depends strongly on the hydrogen bond strength at higher temperatures. The inertial component becomes independent of hydrogen bond strength at low temperatures. The loss of correlation at lower temperatures is caused by the increased importance of collective effects of the extended hydrogen bonding network. Using a new harmonic cone model, the experimentally measured amplitudes of the inertial decays yielded values of the characteristic frequencies of the intermolecular angular potential for various strengths of hydrogen bonds. The frequencies are in the range of ~400 cm<sup>-1</sup>.

### **c. Orientational and Translational Dynamics of Polyether/Water Solutions<sup>11,12</sup>**

Optical heterodyne-detected optical Kerr effect (OHD-OKE) experiments and pulsed field-gradient spin-echo NMR (PFGSE-NMR) experiments were performed to measure the rotational and translational diffusion constants of a polyether, tetraethylene glycol dimethyl ether (TEGDE), in binary mixtures with water over concentrations ranging from pure TEGDE to approaching infinite dilution. In addition, hydrodynamic calculations of the rotational and translational diffusion constants for several rigid TEGDE conformations in the neat liquid and in the infinitely dilute solution were performed to supplement the experimental data. The temperature dependence of the rotational and translation dynamics of TEGDE were also measured and compared to the water concentrations dependence. TEGDE is a model for PEO, a very important polyether with hydroxyl terminal groups that is important in many medical and industrial applications. The results demonstrate that, in contrast to reports in the literature, there are no large TEGDE structural changes or specific, long-lived water-polyether interactions in the solutions over the entire concentration range. The behavior of TEGDE as water is added is discussed using a free volume picture.

### **B. Investigations of Room Temperature Ionic Liquids**

#### **1. Dynamics in Organic Ionic Liquids in Distinct Regions<sup>13</sup>**

The temperature-dependent fluorescence anisotropy decay (orientational relaxation) of perylene and sodium 8-methoxypyrene-1,3,6-sulfonate (MPTS) were measured in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (alkyl = ethyl, butyl, hexyl, octyl) room temperature ionic liquids (RTIL). The two fluorescent probe molecules display markedly different rotational dynamics when analyzed using Stokes-Einstein-Debye theory demonstrating that they are located in distinct environments within the RTILs and have very different interactions with their surroundings. As the length of ionic liquid alkyl chain is increased the perylene dynamics approach those of perylene in an organic oil. In contrast, MPTS shows behavior reflecting very strong coordination with the RTIL cations. The results were related to various chemical and physical processes that occur in RTILs.

#### **2. Optical Heterodyne Detected Optical Kerr Effect Experiments<sup>14</sup>**

The addition of lithium salts to RTILs causes an increase in viscosity and decrease in ionic mobility, the understanding of which is important in RTILs possible applications as alternative solvents in lithium ion batteries. OHD-OKE spectroscopy was used to study the change in dynamics, principally orientational relaxation, caused by the addition of lithium bis(trifluoromethylsulfonyl)imide to the ionic liquid 1-butyl 3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The lithium salt concentration was found to affect the dynamics on multiple time scales and discontinuities in the observables were found when the concentration (mole fraction) of lithium salt is close to  $\chi(\text{LiTf}_2\text{N}) = 0.2$ . It was found that

the dynamics are described very well by mode coupling theory. The change in dynamical behavior at  $\chi(\text{LiTf}_2\text{N}) = 0.2$  was discussed in terms of structural changes in the solvation of the lithium cations.

### **C. Studies of Interfaces and Surfaces<sup>15</sup>**

A main thrust of the current proposal is to develop and apply 2D IR vibrational echo spectroscopy to the study of dynamics and molecular interactions at interfaces and surfaces. Ultrafast two-dimensional infrared vibrational echo spectroscopy has proven broadly useful for studying molecular dynamics in solutions. We have extended the technique to probing the interfacial dynamics and structure of a silica surface-tethered transition metal carbonyl complex – tricarbonyl (1,10-phenanthroline)rhenium chloride – of interest as a photoreduction catalyst. We interpret the data using a theoretical framework devised in the Fayer group to separate the roles of structural evolution and excitation transfer in inducing spectral diffusion. The structural dynamics, as reported on by a carbonyl stretch vibration of the surface-bound complex, have a characteristic time of ~150 picoseconds in the absence of solvent, decrease in duration by a factor of three upon addition of chloroform, and decrease another order of magnitude for the bulk solution. Conversely, solvent-complex interactions increase the lifetime of the probed vibration by 160% when solvent is applied to the monolayer. These are the first measurement of the structural dynamics of molecules on any surface. These experiments and the future experiments in this area will greatly extend our understanding of molecules on surfaces and will elucidate totally new aspects of how heterogeneous catalysts function;